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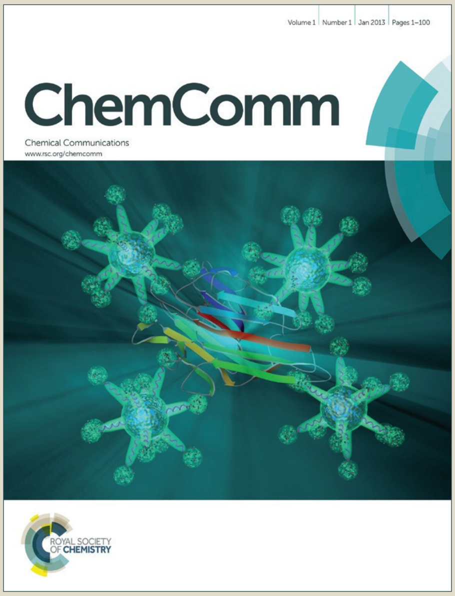

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Insertion of phenyl isothiocyanate into a P–P bond of a nickel-substituted bicyclo[1.1.0]tetraphosphabutane

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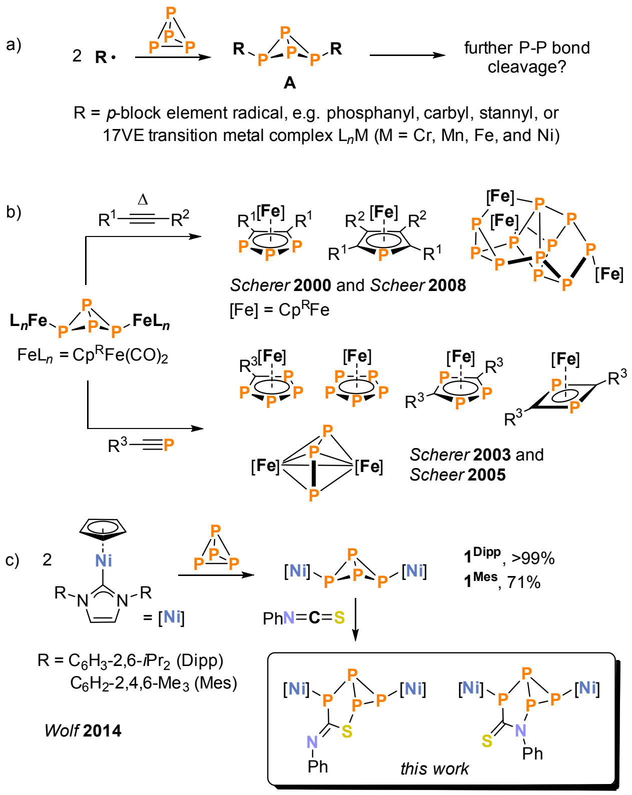
A new reaction mode for bicyclo[1.1.0]tetraphosphabutanes is reported. The C=S and C=N bonds of phenyl isothiocyanate reversibly insert into a P–P bond of [{CpNi(IMes)}$_2$(μ-η^1:η^1-P$_4$)] (1^{Mes}, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene), forming isomers 2a and 2b. X-ray crystallography and ^{31}P{^{1}H} NMR spectroscopy revealed similar bicyclo[3.1.0]heterohexane structures for these compounds.

Developing new, targeted and selective methods for the functionalisation of the P$_4$ molecule remains a topical challenge despite the extensive research efforts carried out in the past.[1,2] Recent reports have focused on the use of nucleophilic carbanions and carbenes,[3,4] insertion reactions of *p*-block elements, e.g. phosphenium cations[5] and the use of main group element or transition metal-based radicals.[6,7] The latter approach often gives rise to bicyclo[1.1.0]tetraphosphabutanes **A**, which may be seen as potential intermediates on the way to a stepwise P$_4$ degradation sequence (Scheme 1a). While various "P$_4$ butterfly" compounds of type **A** are known, it is interesting to note that their reactivity has only been explored to a small extent.[1,6–9] Previous studies mainly focused on iron complexes.[1d,7a,7c,9–11] As reported by Scherer and Scheer, thermolysis or photolysis of [(Cp^{R}Fe(CO)$_2$)$_2$(μ-η^1:η^1-P$_4$)] (Cp^R = C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_9$H$_5$-1,3-*t*Bu$_2$ and C$_5$*i*Pr$_5$) affords mixtures of polyphosphido complexes.[7a,c] Reactions with (phospha)alkynes evoked the P$_3$/P$_1$ fragmentation of the bicyclo[1.1.0]tetraphosphabutanediyl fragment, forming phosphide, phospholide, diphosphacyclobutadiene components.[9,10] Further studies revealed that the "P$_4$ butterfly" may be protonated reversibly and coordinates as a chelate ligand to copper(I).[11] Here, we disclose a new reaction mode for metal-substituted bicyclo[1.1.0] tetraphosphabutanes. We have found that phenyl isothiocyanate reversibly inserts into a P–P bond of the bicyclo[1.1.0]tetraphosphabutane scaffold of the dinuclear nickel complex [{(η^5-Cp)Ni(IMes)}$_2$(μ-η^1:η^1-P$_4$)] (1^{Mes}, Scheme 2b).[7b] This unprecedented reaction affords the isomers **2a** and **2b**, which display a bicyclo[3.1.0]heterohexane skeleton. We de-



Scheme 1. a) Formation of bicyclo[1.1.0]tetraphosphabutanes amenable for further transformations; b) Selected reactions of iron-substituted bicyclo[1.1.0]tetraphosphabutanes; Cp^R = C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_9$H$_5$-1,3-*t*Bu$_2$, C$_5$*i*Pr$_5$, R^1 = R^2 = Me, Ph; R^1 = H, R^2 = Ph, *t*Bu, SiMe$_3$, CO$_2$Me/Et, R^3 = *t*Bu, C(CH$_2$)$_5$Me; c) synthesis of **1**^{Dipp} and **1**^{Mes} and reactivity toward phenyl isothiocyanate.[6–10]

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scribe the single-crystal X-ray structures and $^{31}P\{^1H\}$ NMR data of these new complexes and analyse the possible nature of additional reaction products using DFT calculations.

We recently synthesised of the first nickel-substituted bicyclo[1.1.0]tetraphosphabutane, $[\{(\eta^5\text{-Cp})Ni(IDipp)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$ (**1^{Dipp}**, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene).[7b] This complex is formed in a quantitative reaction from two equivalents $[(\eta^5\text{-Cp})Ni(IDipp)]$ and P_4 (Scheme 1c). Subsequent work showed that the slightly less encumbered mesityl-substituted complex $[\{(\eta^5\text{-Cp})Ni(IMes)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}P_4)]$ (**1^{Mes}**) is obtained in an analogous fashion. **1^{Mes}** was isolated as dark red air-sensitive crystals in 71% yield (Scheme 1c) and shows a better solubility than **1^{Dipp}**, dissolving well in benzene, toluene, diethyl ether and tetrahydrofuran.†

In order to probe the reactivity of **1^{Dipp}** and **1^{Mes}**, we investigated reactions with heteroallenes. ADMX spin systems were observed by ^{31}P NMR spectroscopy with CS_2 (10 equiv.), suggesting an insertion into a P–P bond, but the products could not be isolated.† Isolable products were obtained with phenyl isothiocyanate, however. Monitoring the reaction of **1^{Mes}** and PhNCS in [D$_8$]THF (Fig. 1) revealed that 7 equiv. PhNCS were necessary for full conversion of **1^{Mes}** after four hours, while a large amount of **1^{Mes}** (55%) remained in the reaction mixture with one equiv. PhNCS after one day (Figure S8, ESI).Two main products **2a** and **2b** (ADMX spin systems) and one minor species **2c** were detected (approximate ratio **2a**:**2b**:**2c** 75:20:5).‡ The simultaneous formation of **2a**, **2b** and **2c** commences below 0 °C according to a VT NMR study ([D$_8$]THF, Fig. S8, ESI). Prolonged reaction times and heating of the solution resulted in essentially the same product ratio, although the signal to noise ratio of the spectra decreased over time. In contrast, the $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1^{Dipp}** with a large excess of PhNCS in [D$_8$]THF after two days at room temperature showed signals of a species similar to **2b** (15%, ADMX spin system), **1^{Dipp}** (50%) and P_4 (35%) (Fig. S9,ESI).

Complex **2a** can be isolated as an analytically pure, dark brown solid in 31% yield by crystallising the crude product twice from toluene/*n*-hexane.† Crystallisation of the crude product from diethyl ether and recrystallization from toluene/*n*-hexane affords pure, crystalline **2b** in 16% isolated yield. Single-crystal XRD for **2a** (Fig. 2, top) revealed an unusual nickel-substituted bicyclo[3.1.0]-2-thia-1,4,5,6-tetraphosphahexane moiety (P1–C1 1.860(4) Å, P4–S1 2.1257(13) Å) with an exocyclic imino function. The C1–N1 (1.278(5) Å) and S1–C1 (1.795(5) Å) bonds of **2a** are elongated compared to free aryl isothiocyanates.[12] The P–P distances (2.1818(14) – 2.2222(14) Å) are in the range of single bonds.[7] The five-membered CP_3S heterocycle (P1–P2–P4–S1–C1) is almost flat (Σ_{angles} = 535.8°) and orthogonal (89.60(7)°) to the plane formed by P2, P3 and P4. The scaffold of **2a** is analogous to that of 2,3,4,6-tetra-*tert*-butylbicyclo[3.1.0]hexaphosphane synthesised by Baudler *et al.*.[13]

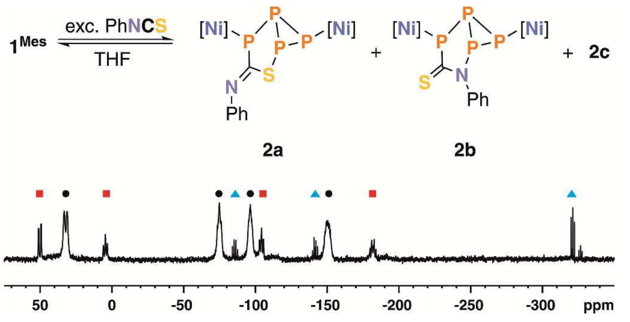

Fig. 1. Synthesis of **2a** and **2b** (top), and $^{31}P\{^1H\}$ NMR spectrum ([D$_8$]THF) of the reaction of PhNCS and **1^{Mes}** (7:1) at room temperature after four hours; ● = **2a**, ■ = **2b**, ▲ = **2c** (bottom).

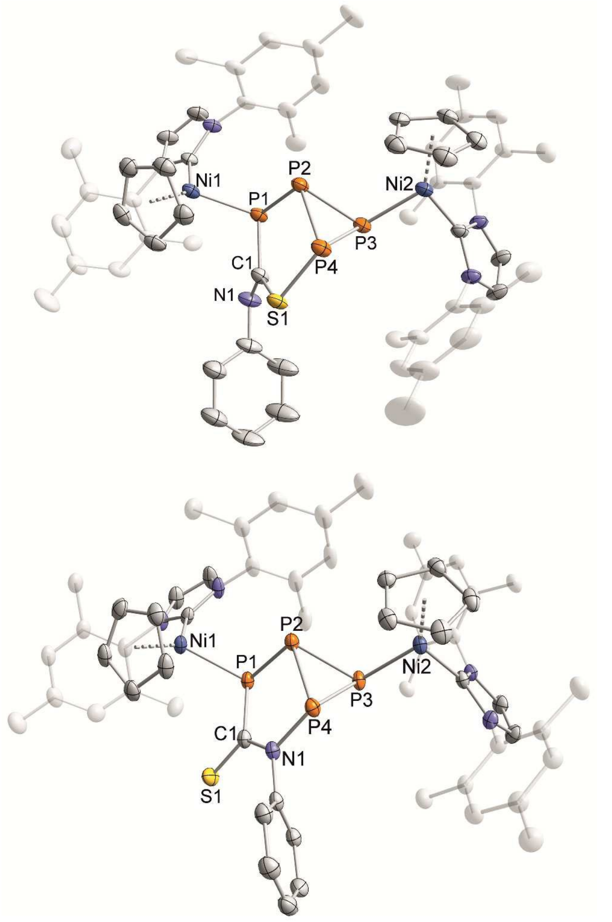

Fig. 2. Solid-state molecular structures of **2a** (top) and **2b** (bottom). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% level. Selected bond lengths [Å] and angles [°] for **2a**: P1–C1 1.860(4), P4–S1 2.1257(13), P1–P2 2.1818(14), P2–P3 2.2182(15), P2–P4 2.2222(14), P3–P4 2.1935(15), C1–S1 1.794(4), C1–N1 1.278(6), Ni1–P1 2.2036(13), Ni2–P3 2.1906(11), P1–P2–P4 102.89(5), P2–P4–S1 102.86(6), P4–S1–C1 104.82(14), S1–C1–P1 122.3(2), C1–P1–P2 102.88(14), P3–P2–P4 59.20(5), P1–C1–N1 116.4(3), S1–C1–N1 121.3(2); for **2b**: P1–C1 1.828(3), P4–N1 1.785(3), P1–P2 2.2157(11), P2–P4 2.1969(10), P2–P3 2.2233(10), P3–P4 2.206(1), C1–N1 1.359(4), C1–S1 1.678(3), Ni1–P1 2.2188(9), Ni2–P3 2.2192(9), P1–P2–P4 95.28(4), P2–P4–N1 99.75(9), P4–N1–C1 124.9(2), N1–C1–P1 118.6(2), C1–P1–P2 100.48(3), P3–P2–P4 59.88(3), P1–C1–S1 117.68(18), N1–C1–S1 123.6(2).

The molecular structure of the regio isomer **2b** (Fig. 2, bottom) features a flat CNP_3 heterocycle (Σ_{angles} = 539.0°) with a thioketone function (C1–S1 1.678(3) Å) and single bonds between P1–C1 (1.828(3) Å) and P4–N1 (1.785(3) Å). The P–P distances in **2b** (2.1969(10) – 2.2233(10) Å) are similar to those of **2a**.

The CNP_3 ring forms an acute dihedral angle of 79.58(5)° with the P2–P3–P4 plane.

The $^{31}P\{^1H\}$ NMR spectrum of **2a** ($[D_8]THF$, room temperature) features four broad multiplets at −150.1, −96.4, −75.0 and 32.1 ppm consistent with four chemically different P atoms. The signals are broad at room temperature (average half-width τ_{FWHM} = 565 Hz); they become sharper when the temperature is decreased to −80 °C (av. τ_{FWHM} = 35 Hz). Experimental and fitted $^{31}P\{^1H\}$ NMR spectra in $[D_8]THF$ at −80 °C along with the assignment of the chemical shifts and coupling constants are shown in Fig. 3. The resonance at −151.8 ppm is assigned to P_A connected to three P atoms based on the observation of three large $^1J(P,P)$-coupling constants for this multiplet ($^1J(P_AP_D)$ = −178 Hz, $^1J(P_AP_M)$ = −185 Hz and $^1J(P_AP_X)$ = −374 Hz). The P atoms coordinated to nickel ($\delta(P_D)$ = −105.5 ppm; $\delta(P_X)$ = 27.8 ppm) show a common large $^2J(P,P)$ coupling ($^2J(P_D,P_X)$ = 82 Hz), which may arise from an interaction of the lone pairs due to the conformational constraints of the bicyclo[3.1.0]heterohexane skeleton.[13]

Complex **2b** gives rise to four slightly broad $^{31}P\{^1H\}$ NMR resonances at −182.1, −104.5, 4.5 and 50.1 ppm in $[D_8]THF$ at room temperature. The line width decreased from an average of τ_{FWHM} = 33 Hz at room temperature to τ_{FWHM} = 23 Hz upon cooling to −80 °C. The chemical shifts and coupling constants of **2b** lie in a similar range as observed for **2a** (Fig. 3, bottom) in agreement with the similar structure motif.

$^{31}P\{^1H\}$ NMR studies indicate that the formation of **2a**, **2b** and **2c** is reversible; i.e. the products slowly equilibrate with the starting material $\mathbf{1}^{\mathbf{Mes}}$ in solution.† A mixture of **2a** (89%), $\mathbf{1}^{\mathbf{Mes}}$ (7%), **2c** (4%) and **2b** (traces) was detected upon storing a $[D_8]THF$ solution of pure **2a** in an NMR tube at room temperature for two days, while a 65:10:5:20 mixture (**2a**:**2b**:**2c**:$\mathbf{1}^{\mathbf{Mes}}$) was present after one week.§ Additional multiplets of unidentified minor species can be observed upon prolonged storage (Figure S11, ESI).† **2b** behaves similarly (Figure S12). IR monitoring of the decomposition of **2a** ($[D_8]THF$, 60 °C, 13.5 hours) shows the formation of free PhNCS (Fig S13, ESI).

DFT calculations (ωB97X-D/6-311G(d,p) level)[14] were performed to gain additional insight into the thermodynamics of the reaction. The optimized structures of the truncated model complexes $\mathbf{1}^{\mathbf{Ph}}$, $\mathbf{2a}^{\mathbf{Ph}}$ and $\mathbf{2b}^{\mathbf{Ph}}$, where the Mes substituents were replaced by phenyl groups for computational efficiency, are in good agreement with the experimental structures (Fig. 4a). The formation of $\mathbf{2a}^{\mathbf{Ph}}$ and $\mathbf{2b}^{\mathbf{Ph}}$ is exergonic, and the thermodynamic product of the reaction appears to be $\mathbf{2b}^{\mathbf{Ph}}$ (−15.2 kcal/mol with respect the starting materials), while $\mathbf{2a}^{\mathbf{Ph}}$ (−11.3 kcal/mol) is a kinetic product.§§

In conclusion, the reaction of $\mathbf{1}^{\mathbf{Mes}}$ with PhNCS affords the novel complexes **2a** and **2b** with an unusual bicyclo[3.1.0]heterohexane skeleton. To our knowledge, this represents the first example of an insertion of a heteroallene into a P–P bond of a cyclopolyphosphane. In future work, it will be of interest to investigate whether similar reactions with polar multiple bonds offer a general route toward “functionalized” polyphosphanes.[16] Efficient preparative methods exist for a range of bicyclo[1.1.0]tetraphosphabutanes,[1,6–9] therefore, such transformations may provide a fruitful avenue to the stepwise and selective degradation of the P_4 molecule.

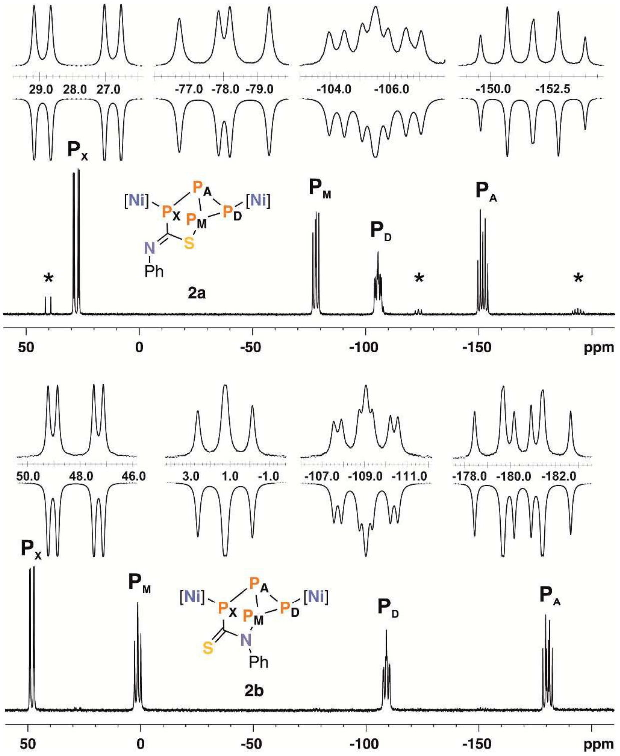

Fig. 3 $^{31}P\{^1H\}$ NMR spectra of **2a** (top) and **2b** (bottom, 161.98 MHz, $[D_8]THF$, 193 K); **2a** (ADMX spin system): δ_A = −151.8 ppm, δ_D = −105.5 ppm, δ_M = −78.0 ppm, δ_X = 27.8 ppm, $^1J(P_AP_D)$ = −178 Hz, $^1J(P_AP_M)$ = −185 Hz, $^1J(P_AP_X)$ = −374 Hz, $^1J(P_DP_M)$ = −238 Hz, $^2J(P_DP_X)$ = 82 Hz, $^2J(P_MP_X)$ = 9 Hz; **2b** (ADMX spin system): δ_A = −180.5 ppm, δ_D = −109.1 ppm, δ_M = 1.2 ppm, δ_X = 48.2 ppm, $^1J(P_AP_D)$ = −193 Hz, $^1J(P_AP_M)$ = −209 Hz, $^1J(P_AP_X)$ = −282 Hz, $^1J(P_DP_M)$ = −237 Hz, $^2J(P_DP_X)$ = 57 Hz, $^2J(P_MP_X)$ = 10 Hz; Expansions (inset) show the experimental (up) and fitted spectra (down). The signals assigned to **2b** are labeled with an asterisk.

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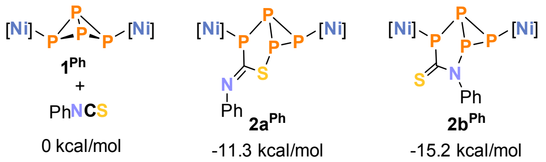

Figure 4. a) Calculated, relative Gibbs free energies (kcal/mol) of $\mathbf{1}^{\mathbf{Ph}}$, $\mathbf{2a}^{\mathbf{Ph}}$ and $\mathbf{2b}^{\mathbf{Ph}}$. The relative Gibbs free energies refer to $\mathbf{1}^{\mathbf{Ph}}$ + PhNCS (kcal/mol).

Notes and References

‡$^{31}P\{^1H\}$ NMR data of **2c** ($[D_8]THF$, A_2MX spin system): δ = −321.2 (dd, 2P, P_A, $^1J(P_AP_M)$ = −178 Hz, $^1J(P_AP_X)$ = −188 Hz), −141.5 (dt, 1P, P_M, $^2J(P_MP_X)$ = 208 Hz), −85.8 (dt, 1P, P_X) ppm.

§The ^1H NMR spectrum of a freshly prepared $[D_8]THF$ solution of pure crystals of **2a** stored for one week at room temperature in an Ar-filled glove box also showed a mixture containing **2a**, **2b** and $\mathbf{1}^{\mathbf{Mes}}$ in a 94.5:0.5:5 ratio.

§§The structure and the mechanism of formation of the minor product **2c** (A_2MX spin system, *vide supra*) presently remains unclear. Five potential candidates were identified by our computations (Fig. S14, ESI).† These calculated isomers are adducts of the starting material with PhNCS (**2c**$^{\mathbf{Add1}}$ and **2c**$^{\mathbf{Add2}}$) or result from the insertion of the C=S or C=N double bonds into the Ni−P bond ((*E*)-**2c**$^{\mathbf{Ins1}}$, (*Z*)-**2c**$^{\mathbf{Ins1}}$ and **2c**$^{\mathbf{Ins2}}$).[15] Each of them has an energy significantly higher than that of **2a**$^{\mathbf{Ph}}$ and **2b**$^{\mathbf{Ph}}$.

1 Reviews: a) B. M. Cossairt, N. A. Piro and C. C. Cummins, *Chem. Rev.* 2010, **110**, 4164; b) M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Rev.* 2010, **110**, 4178; c) M. Peruzzini, I. de los Rios, A. Romerosa and F. Vizza, *Eur. J. Inorg. Chem.* 2001, **2001**, 593; d) M. Peruzzini, R. R. Abdreimova, Y. Budnikova, A. Romerosa, O. J. Scherer and H. Sitzmann, *J. Organomet. Chem.* 2004, **689**, 4319; e) M. Peruzzini, L. Gonsalvi and A. Romerosa, *Chem. Soc. Rev.* 2005, **34**, 1038.

2 Selected publications on transformations of transition metal phosphide complexes derived from P_4 in one step: a) P. Barbaro, C. Bazzicalupi, M. Peruzzini, S. Seniori Costantini and P. Stoppioni, *Angew. Chem. Int. Ed.* 2012, **51**, 8628; b) E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl and M. Scheer, *Angew. Chem. Int. Ed.* 2014, **53**, 7643.

3 a) W. T. K. Chan, F. García, A. D. Hopkins, L. C. Martin, M. McPartlin and D. S. Wright, *Angew. Chem. Int. Ed.* 2007, **46**, 3084; b) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg and K. Lammertsma, *Angew. Chem. Int. Ed.* 2014, **53**, 12836; c) M. Arrowsmith, M. S. Hill, A. L. Johnson, G. Kociok-Köhn and M. F. Mahon, *Angew. Chem. Int. Ed.* 2015, **54**, 7882; d) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg and K. Lammertsma, *Angew. Chem. Int. Ed.* 2015, **55**, 613.

4 a) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.* 2007, **46**, 7052; b) O. Back, G. Kuchenbeiser, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.* 2009, **48**, 5530.

5 Selected publications on the insertion of *p*-block elements into the P−P bonds of P_4: a) Y. Xiong, S. Yao, M. Brym and M. Driess, *Angew. Chem. Int. Ed.* 2007, **46**, 4511; b) J. J. Weigand, M. Holthausen and R. Fröhlich, *Angew. Chem. Int. Ed.* 2009, **48**, 295; c) M. H. Holthausen and J. J. Weigand, *J. Am. Chem. Soc.* 2009, **131**, 14210; d) G. Prabusankar, A. Doddi, C. Gemel, M. Winter and R. A. Fischer, *Inorg. Chem.* 2010, **49**, 7976; e) M. H. Holthausen and J. J. Weigand, *Chem. Soc. Rev.* 2014, **43**, 6639.

6 a) J.-P. Bezombes, P. B. Hitchcock, M. F. Lappert and J. E. Nycz, *Dalton Trans.* 2004, 499; b) B. M. Cossairt and C. C. Cummins, *New J. Chem.* 2010, **34**, 1533; c) S. Khan, R. Michel, J. M. Dieterich, R. A. Mata, H. W. Roesky, J.-P. Demers, A. Lange and D. Stalke, *J. Am. Chem. Soc.* 2011, **133**, 17889; d) N. A. Giffin, A. D. Hendsbee, T. L. Roemmele, M. D. Lumsden, C. C. Pye and J. D. Masuda, *Inorg. Chem.* 2012, **51**, 11837; e) S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner and M. Scheer, *Angew. Chem. Int. Ed.* 2014, **53**, 7639.

7 a) O. J. Scherer, T. Hilt and G. Wolmershäuser, *Organometallics* 1998, **17**, 4110; b) S. Pelties, D. Herrmann, B. de Bruin, F. Hartl and R. Wolf, *Chem. Commun.* 2014, **50**, 7014; c) S. Heinl and M. Scheer, *Chem. Sci.* 2014, **5**, 3221; d) C. Schwarzmaier, A. Y. Timoshkin, G. Balázs and M. Scheer, *Angew. Chem. Int. Ed.* 2014, **53**, 9077; e) D. W. Agnew, C. E. Moore, A. L. Rheingold and J. S. Figueroa, *Angew. Chem. Int. Ed.* 2015, **54**, 12673.

8 Selected main group element-substituted “butterfly P_4” compounds with an E_2P_4 core: a) E. Niecke, R. Rüger and B. Krebs, *Angew. Chem. Int. Ed. Engl.* 1982, **21**, 544; b) R. Riedel, H.-D. Hausen and E. Fluck, *Angew. Chem. Int. Ed. Engl.* 1985, **24**, 1056; c) S. L. Hinchley, C. A. Morrison, D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. Voigt, A. H. Cowley, M. F. Lappert, G. Gundersen, J. A. C. Clyburne and P. P. Power, *J. Am. Chem. Soc.* 2001, **123**, 9045.

9 a) O. J. Scherer, T. Hilt and G. Wolmershäuser, *Angew. Chem. Int. Ed.* 2000, **39**, 1425; b) C. Eichhorn, *PhD thesis*, Kaiserslautern **2003**; c) S. Deng, C. Schwarzmaier, C. Eichhorn, O. J. Scherer, G. Wolmershäuser, M. Zabel and M. Scheer, *Chem. Commun.* 2008, 4064.

10 M. Scheer, S. Deng, O. J. Scherer and M. Sierka, *Angew. Chem. Int. Ed.* 2005, **44**, 3755.

11 C. Schwarzmaier, S. Heinl, G. Balázs and M. Scheer, *Angew. Chem. Int. Ed.* 2015, **54**, 13116.

12 S. Biswas, S. Haldar, P. K. Mandal, K. Goubitz, H. Schenk and R. Dabrowski, *Cryst. Res. Technol.* 2007, **42**, 1029.

13 a) M. Baudler, Y. Aktalay, K.-F. Tebbe and T. Heinlein, *Angew. Chem. Int. Ed. Engl.* 1981, **20**, 967; in this context see also: b) M. Baudler, *Angew. Chem. Int. Ed. Engl.* 1982, **21**, 492.

14 DFT calculations were performed using Gaussian09; see supporting information for further details.

15 Selected examples for the insertion of isothiocyanates into transition metal−phosphorus bonds: a) U. Segerer and E. Hey-Hawkins, *Polyhedron* 1997, **16**, 2537; b) U. Segerer, J. Sieler and E. Hey-Hawkins, *Organometallics* 2000, **19**, 2445; c) A. Antiñolo, S. García-Yuste, A. Otero and R. Reguillo-Carmona, *Eur. J. Inorg. Chem.* 2009, 539; d) W. Yi, J. Zhang, L. Hong, Z. Chen and X. Zhou, *Organometallics* 2011, **30**, 5809.

16 a) A. R. Jupp and J. M. Goicoechea, *Angew. Chem. Int. Ed.* 2013, **52**, 10064; b) R. S. P. Turbervill and J. M. Goicoechea, *Chem. Commun.* 2012, **48**, 6100; c) R. S. P. Turbervill, A. R. Jupp, P. S. B. McCullough, D. Ergöçmen and J. M. Goicoechea, *Organometallics* 2013, **32**, 2234.